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Facile construction of nanofibrous ZnO photoelectrode for dye-sensitized solar cell applications

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A facile method to prepare nanofibrous ZnO photoelectrodes with tunable thicknesses by electrospinning is reported. A "self-relaxation layer" is formed spontaneously between ZnO nanofibers and fluorine-doped SnO_2 (FTO) substrate, which facilitates the release of interfacial tensile stress during calcination, resulting in good adhesion of ZnO film to FTO substrate. Dye-sensitized solar cells (DSSCs) based on the nanofibrous ZnO photoelectrodes are fabricated and an energy conversion efficiency of 3.02% is achieved under irradiation of AM 1.5 simulated sunlight with a power density of 100 mW cm^{-2}, which shows good promise of electrospun nanofibrous ZnO as the photoelectrode in DSSCs. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3193661]

Dye-sensitized solar cells (DSSCs) are under intensive investigation due to their low fabrication cost and relatively high efficiency compared to conventional silicon solar cells.[1] While most DSSCs utilize nanocrystalline TiO_2 as the photoelectrode, ZnO has proven to be a promising alternative photoelectrode material owing to its similar band gap and comparable electron injection process as that of TiO_2.[2] In addition, ZnO is widely available with high electron mobility.[3] Up to date, the highest efficiency for ZnO-based DSSCs is reported to be 6.58%,[4] which is lower than that for devices based on TiO_2 photoelectrodes. This is due to the poor chemical stability of ZnO in acidic dye solution and the formation of Zn^{2+}/dye complexes that could block the injection of electrons from the dye molecules to the semiconducting electrodes.[5,6] To improve the performance of ZnO-based DSSCs, one strategy is to design new dyes that are suitable for ZnO photoelectrode,[7] and the other is to develop ZnO photoelectrode with new architectures. In this context, one-dimensional (1D) ZnO nanostructures have attracted great interest recently because they could provide a direct conduction pathway for rapid collection of photoelectrons.[8] Up to date, photoelectrodes based on ZnO nanowires, nanorods, and nanotubes have been prepared by various techniques, with energy conversion efficiency of 0.5%–1.6%.[9–11]

Alternatively, electrospinning technique has also provided a simple and cost-effective way to prepare semiconductor oxide with 1D nanostructure.[12] However, the application of electrospun nanofibers in DSSC is limited by the poor adhesion of electrospun nanofibers to the FTO substrate. To solve this problem, various pretreatment methods have been developed.[13–15] In our previous study, we have shown that a buffer layer could be introduced to improve the adhesion of TiO_2 nanofibers to substrate.[16] Recently, the hot press treatment has also been applied to enhance the adhesion of ZnO nanofibers to the FTO substrate. However, the morphology of ZnO nanofibers is greatly affected to yield a device efficiency of 1.34%.[17] In this contribution, we report a facile method to prepare nanofibrous ZnO films with tunable thickness and good adhesion to FTO substrate. The performance of DSSCs based on such nanofibrous ZnO film is evaluated and a maximum energy conversion efficiency of 3.02% is achieved.

The ZnO nanofibers were electrospun from a precursor gel containing 0.5 g of zinc acetate [$Zn(OAc)_2$, >99.8%], 0.2 g of poly(ethylene oxide) (M_w=900 000), 100 μl of acetic acid, 4.5 ml of de-ionized water and 18 ml of ethanol at a flow rate of 0.5 ml h^{-1} and an electric field of 0.6 kV cm^{-1}. The as-spun ZnO nanofibers were collected on cleaned fluorine-doped SnO_2 glasses then calcined at 400 °C for 1 h to remove organic components.

Figure 1(a) shows the scanning electron microscope (SEM) image of as-spun ZnO nanofibers on FTO substrates, which demonstrates that uniform ZnO nanofibers with smooth surfaces are obtained. After calcination, ZnO nanofibers have rough surfaces [Fig. 1(b)], which should be beneficial for dye loading.[18] In addition, the ZnO film is smooth and crack-free [the inset of Fig. 1(b)], indicating its good adhesion to the FTO substrate. The specific surface area of calcined ZnO film is 30.0 m^2/g, obtained by the Brunauer–Emmett–Teller analysis.

As reported in the literature, during calcination process, due to the difference in thermal expansion coefficients between ZnO film and glass substrate, the tensile strain from the substrate affects ZnO film and often results in film cracks and peel off.[19] However, the spontaneous formation of "self-relaxation layer" [Fig. 1(c)] by disintegration of nanofibers that adhere to the FTO substrate forms a buffer layer that releases the tensile stress at the interface of the FTO substrate and ZnO nanofibers, which prevents the subsequent ZnO nanofibers from cracking or peeling off from the substrate.

Figure 1(d) shows the variation in ZnO film thickness with different eletrospinning time. By controlling the electrospinning time, the film thickness could be tuned from 0 to 5 μm, which provides convenience for both photoelectrode

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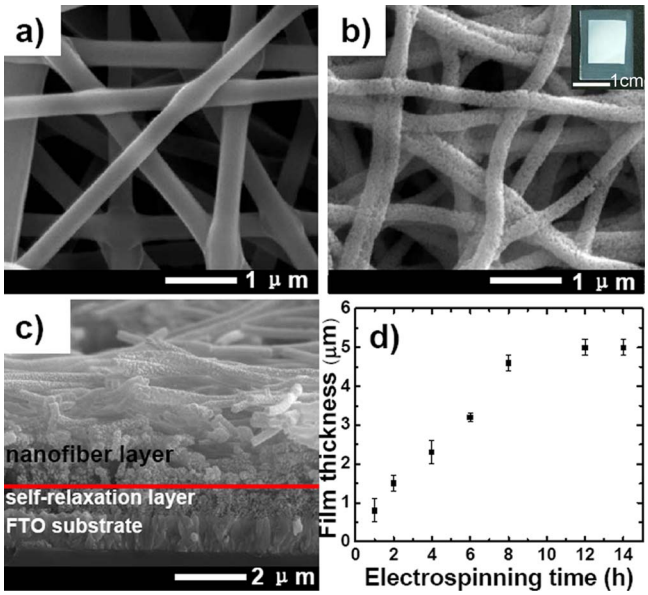

FIG. 1. (Color online) SEM images of the as-spun (a) and calcined (b) ZnO nanofibers on FTO substrates (inset: photograph of calcined ZnO film on FTO substrate). (c) Typical cross-sectional SEM images of the calcined ZnO film on FTO substrate. (d) The variation in ZnO film thickness with different eletrospinning time.

fabrication and understanding the effect of film thickness on DSSC performance.

The crystal structure of ZnO nanofibers was investigated by x-ray diffraction analysis [Fig. 2(a)]. All the peaks are indexed to a wurtzite ZnO phase,[20] which correlate well with the diffraction rings in the selected area electron diffraction pattern [Fig. 2(b)]. These results indicate that ZnO nanofibers with pure wurtzite phase were produced after calcination.

DSSCs based on ZnO nanofibrous photoelectrodes were fabricated by soaking the ZnO films in 0.5 mM N719 solution (Solaronix) dissolved in a 1:1 volume mixture of acetonitrile and tert-butanol for 30 min at room temperature in the dark. Pt-sputtered FTO glass was used as the counterelectrode. The cell area is 0.15 cm^2. 0.1*M* LiI, 0.05*M* I_2, 0.5*M* 4-tert-butylpyridine, and 0.6*M* 1-propyl-2,3-dimethyl imidazolium iodide dissolved in 3-methoxypropylnitrile was used as an electrolyte solution. The typical photocurrent density-voltage curves for these DSSCs under irradiation of AM 1.5 simulated sunlight with a power density of 100 mW cm^{-2} are shown in Fig. 3.

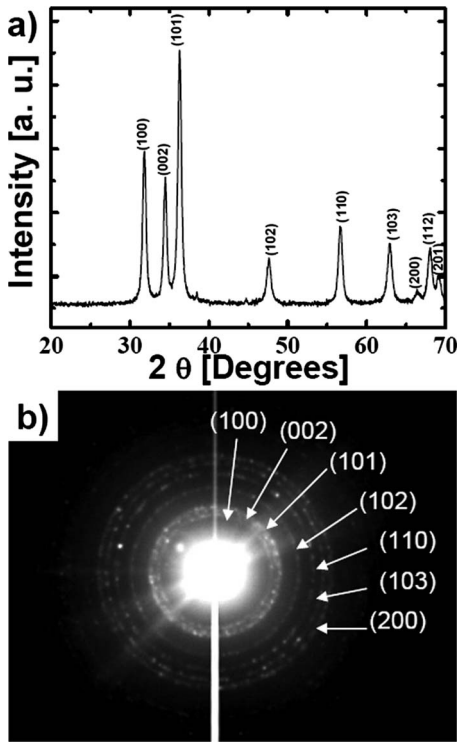

FIG. 2. XRD pattern (a) and selected area diffraction pattern (b) of the calcined ZnO nanofibers.

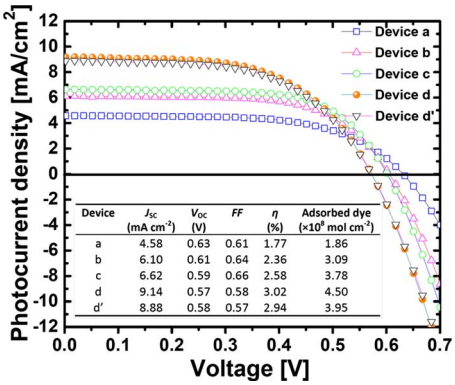

FIG. 3. (Color online) Typical photocurrent density-voltage curves of DSSCs made of ZnO nanofibrous photoelectrodes with a film thickness of 1.5 μm (a), 3.2 μm (b), and 5.0 μm (c), without $Zn(OAc)_2$ solution treatment. (d) Film thickness of 5.0 μm with $Zn(OAc)_2$ solution treatment; (d′) same as device d with reduced dye soaking time to 20 min.

From Fig. 3, it is evident that the energy conversion efficiency (η) is improved with increased ZnO film thickness and a maximum energy efficiency of 2.58% is observed for device (c) with a film thickness of ~5.0 μm. The improved cell performance with increased film thickness is mainly attributed to the improvement in short-circuit current density (J_{sc}), which can be explained by the larger surface area of the ZnO film with increased thickness and thus higher dye loading. The dye loading was determined by desorbing the dye in 1 mM KOH aqueous solution and measuring the UV-visible absorption spectrum at 500 nm. The cell performance of device (c) was further improved by treating the calcined ZnO film with 0.2*M* $Zn(OAc)_2$ aqueous solution for 5 min, calcining again at 400 °C for 30 min and then soaking in 0.5 mM N719 solution for 30 min, yielding the η of 3.02% for device (d). This efficiency is attractive considering the film thickness is only 5 μm and no scattering layer is added.[4] For device (d), the dye loading is also increased by 19% as compared to that for device (c) under similar experimental conditions, which indicates that there is an increase in surface area of the photoelectrode upon $Zn(OAc)_2$ treatment.

To understand the improved cell performance by $Zn(OAc)_2$ treatment, the devices with and without $Zn(OAc)_2$ treatment were further investigated by electrochemical impedance spectroscopy.[21] In addition, to minimize the effect of increased dye loading in device performance, the device (d′) was fabricated by adjusting the dye soaking time to ~20 min to yield a similar dye loading as compared to that of device (c).

The Nyquist plots [Fig. 4(a)] show that the radius of the right semicircle of the device (d′) is apparently larger than that of the device (c). This indicates that the electron recombination resistance increases after $Zn(OAc)_2$ solution

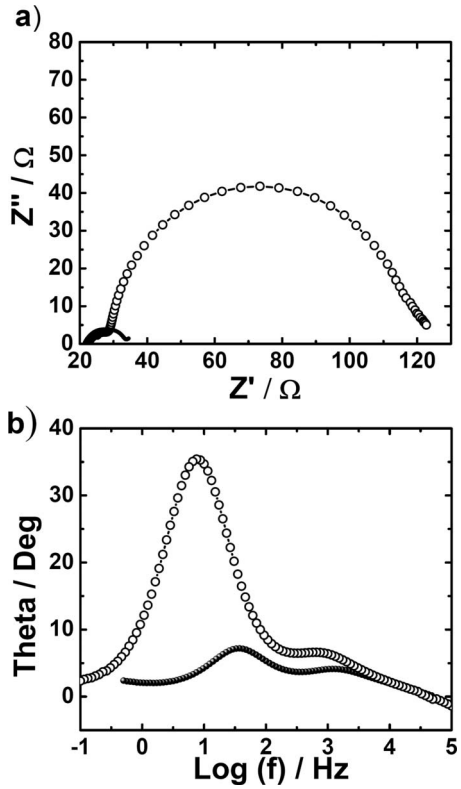

FIG. 4. Impedance spectra of DSSCs made of ZnO nanofibrous photoelectrodes with (open circles) and without (filled circles) $Zn(OAc)_2$ aqueous solution treatment, measured at –0.70 V bias in the dark. (a) Nyquist plots. (b) Bode phase plots.

treatment.[21] From Bode phase plots [Fig. 4(b)], the frequency of the peak in the middle-frequency region (f_{mid}) is 37.4 Hz for device (c) and 7.55 Hz for device (d′). Using the equation of $\tau_e = 1/2\pi f_{mid}$,[22] the electron lifetime (τ_e) values are calculated to be 4.3 and 21 ms for devices (c) and (d′), respectively. The longer electron lifetime for device (d′) indicates more effective suppression of the back reaction between photoelectrons in the conduction band of ZnO and I_3^- in the electrolyte,[23,24] which is reflected in the improvement of photocurrent and energy conversion efficiency in device (d′). Considering the similar dye loading for devices (c) and (d′) (Fig. 3), the improved cell performance for device (d′) is thus mainly attributed to the more effective suppression of the back reaction for device (d′) relative to that for device (c).

In summary, we present a facile method to prepare nanofibrous ZnO photoelectrodes with tunable thicknesses and good adhesion to FTO substrate. The best device has an energy conversion efficiency of 3.02% with $Zn(OAc)_2$ treatment, which is greatly improved as compared to the previous report.[17] These results show good promise of electrospun nanofibrous ZnO as the photoelectrode in DSSCs.

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